7C, 10B/2002G104

Structural Change of Surfactants in Forming of Metal Colloids in the Emulsions

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Introduction

Reverse micelles are well known to be spherical water pools in oil, that is, w/o microemulsions. By collisions these pools exchange their water contents and again form two independent pools. This process has been used to make nanosized material by either chemical reduction of metal ions or coprecipitation reactions [1]. Under this reaction, the solvation structure of these water pools might be so instable that it has not been well understood. On the other hand, gold and silver colloidal particles can be synthesized by photo-reduction of $HAuCl_4·4H_2O$ and $AgNO_3$ in w/o microemulsions, respectively [2]. The aim of this study is to determine the solvation structure of Au^{3+} (or Ag^+) and Br^- in w/o microemulsions with various surfactants, and to investigate the change of solvation structure in the photo-reduction process. In this report, we demonstrate the result of EXAFS analysis for the solvation structure of Br^- with metal ions in the w/o microemulsions.

Experimental

NaBr solutions (333 mM) dissolving two kinds of surfactants [cationic and nonionic] were composed of 8.3 vol% distilled water, 41.7 vol% petroleum solvent, and 50 vol% surfactants, as shown in Table 1. The volume ratio of cationic to nonionic surfactant was 5 to 1. 0.48mol/L Au^{3+} or Ag^+ ions (0.5mL) was then dissolved into these NaBr solutions (12mL) to investigate the effect of metal ions to the size of water pools in the w/o microemulsions. All the surfactants were kindly provided from Nikka Co. Ltd. Those samples were then poured into cells for EXAFS measurements.

Br-K edge EXAFS spectra were collected at the BL-7C and/or BL-10B. The EXAFS measurements were carried out at room temperature in a transmission mode to estimate the coordination numbers around Br^- in the water pools with and without metal ions in w/o microemulsions.

Results and Discussion

Figure 1(a) shows the Br-K edge EXAFS Fourier transforms for NaBr solutions with Au^{3+} ions, compared with that for 500 mM NaBr aqueous solution. Due to the addition of cationic and nonionic surfactants, the height of main peak assigned to Br-O and/or Br-C bond decreases. This indicates that the number of water molecules around Br^- ion decreases, and thus leads to the decrease of the average size of individual water pool. By the addition of Au^{3+} ions, moreover, the height of main peak further decreases, and shifts to the longer bond distance R. This means the decreasing contributions of hydrated bromide ions, probably due to the strong interaction between Br^- and Au^{3+} ions.

Figure 1(b) shows the Br-K edge EXAFS Fourier transforms for NaBr solutions with Ag^+ ions. The height of main peak decreases owing to the addition of surfactants and Ag^+ ions, as is similar to the addition of Au^{3+}. However, the shift of main peak against bond distance does not appear, so that the interaction between Br^- and Ag^+ ions is weaker than that between Br^- and Au^{3+}.

Moreover, the photo-reduction of Ag^+ induces no change of the height of the main peak, which indicates the interaction between Br^- and Ag^+ might be the same as that between Br^- and metallic Ag^0. The detailed analysis is in progress.

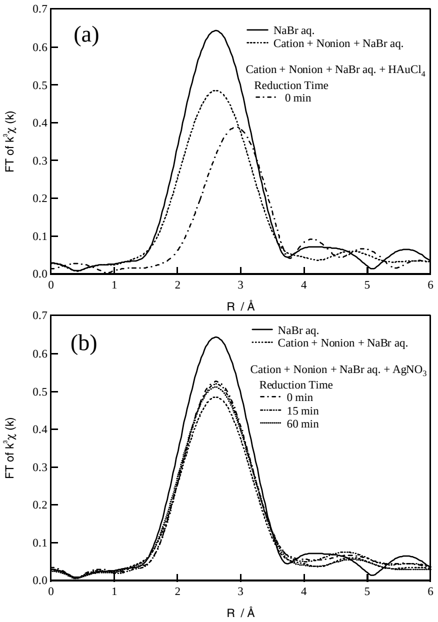

Fig.1 Fourier transforms of Br-K edge for the mixture of cationic and nonionic surfactant solutions containing Br^- with (a) Au^{3+} and (b) Ag^+ ions.

Table 1. Surfactants used in this experiment

Surfactant	Molecular formula
Cationic	$(C_{18}H_{32})_2CH_3\text{-}N^+\text{-}CH_2CH_2OH\ X^-$
Nonionic	$C_{12}H_{25}\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_9\text{-}H$

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